DIELECTRIC ABSORPTION OF 7.7 mm MICROWAVES IN SOME POLAR LIQUIDS

Part I—Alkyl Benzenes

J. BHATTACHARYYA, S. B. ROY AND G. S. KASTHA

OPTICS DEPARTMENT, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA-32

(*Received October 7, 1964*)

ABSTRACT. Measurements on dielectric loss (tan δ) at 38.8 KMc/s have been carried out on toluene, ethyl benzene, isopropyl benzene, *o*-xylene and *m*-xylene in the liquid state at different temperatures. Debye equation for solutions between tan δ and τ has been changed into an expression between tan δ and η with the help of the rate equations in the form

$$\frac{T \tan \delta}{c\mu^2} \quad \frac{(\varepsilon+2)^2}{\varepsilon} \cdot \frac{4\pi N\alpha\omega}{27k} \quad \frac{\eta^\gamma}{1+\alpha^2\omega^2\eta^{2\gamma}}$$

The applicability of the Debye equation has been justified in the case of pure liquids having dipole moments less than 1 D. from the superposition of the plots of $\frac{T \tan \delta}{c\mu^2}$ (tan δ obtained experimentally) vs η over the theoretical curves derived from the left hand side expression of the above equation with $\gamma = 1$ and suitable values of α.

The values of relaxation time, the activation energies for viscous flow and dielectric relaxation have been determined. It has been found that the volumes of the rotors at any temperature for the various alkyl benzenes calculated with the help of the Debye relation between τ and η do not show any quantitative correlation with the molar volumes of the respective compounds at the corresponding temperatures.

INTRODUCTION

The validity of the Debye expression for dielectric loss (tan δ) accompanying absorption of microwaves by polar molecules in dilute solutions in nonpolar solvents, where dipole-dipole interactions could be expected to be negligible, has been well established. But in the case of pure liquids the stronger dipolar interactions render the applicability of the Debye expression uncertain. However, in the case of pure liquids having molecules with small dipole moments the dipolar interactions will be weaker. Whiffen and Thompson (1946) studied the absorption of microwaves of wavelength 1.27 cm in toluene, *o*-xylene and a few other organic compounds in the pure liquid state. They considered the liquids as cent-percent solutions in non-polar solvents and using the Debye equation determined the dipole moments which were in agreement with the (corresponding) literature values. Petro and Smyth (1957) on the other hand measured dielectric constants

and losses at wavelengths 1.25 cm, 3.22 cm and 10 cm at three different temperatures in the case of some alkyl benzenes and other polar organic compounds in the pure liquid state and determined the values of λ_m at these temperaures for all these compounds by using Cole-Cole arc plot method. They discussed the dependence of relaxation times and viscosities on molecular shapes and sizes. Whiffen and Thompson as well as Petro and Smyth tacitly assumed the validity of the Debye expression for dielectric loss for all the polar liquids studied by them.However, though the values of dipole moments obtained by the authors from the Debye equation are in fair agreement with each other, the values of τ for a certain compound at a certain temperature are quite different. As the conclusions arrived at by these authors about molecular size and other molecular properties would depend upon the correctness of the values of τ, it would be desirable to test the accuracy of the value of λ_m reported by Petro and Smyth. For this purpose the measurements in the present case have been made at still higher microwave frequencies so that the maximum absorption in the alkyl benzenes which is expected to occur within a range of 100°C may be observed experimentally. Moreover, as the study of the pure liquids is likely to provide new data about the packing of molecules in the state of aggregation, where the "solvent effect" in dilute solutions (Müller, 1932; Jenkins, 1936) could be avoided, a careful study of the applicability of the Debye equation in the case of pure liquids is necessary. Even the deviations from the validity of the equation may bring out the degree of importance of dipolar interactions in the pure liquids and may throw light on the structure of liquids. With these objects in view , a programme of work was undertaken to investigate the dielectric loss in the still lower microwave region (7.7 mm) in the case of some polar liquids having widely different dipole moments. The present paper discusses the results obtained with some polar benzene derivatives in the pure liquid state, where the values of the dipole moments of the molecules lie within a limit of one Debye unit.

EXPERIMENTAL

The polar liquids studied in the present investigation are toluene, ethyl benzene, isopropyl benzene, *o*-xylene and *m*-xylene. All the chemicals, obtained from reputed firms, were of chemically pure quality. These were first fractionated and the proper fractions were repeatedly distilled under reduced pressure and dried by usual methods before being used in the investigations. The experimental arrangement for the determination of dielectric loss was the same as described in an earlier paper (Bhattacharyya *et al.*, 1964). Absorption of microwaves (38.8 K Mc/s) by the pure liquids taken in a U-shaped cell was measured at different temperatures in terms of *db*, which were then converted into tan δ-values. In the case of all the polar compounds absorption maxima were obtained within the range of temperature variations produced in the bath. The values of the static dielectric constants at different temperatures were taken from the Inter-

national Critical Tables. The values of viscosity and density at different temperatures for all the compounds excepting isopropyl benzene were taken from the Landolt Börnstein Tables, while those for isopropyl benzene were determined experimentally.

RESULTS AND DISCUSSION

The values of the dielectric loss (tan δ) for all the polar liquids at different temperatures along with the corresponding macroscopic viscosity η, time of relaxation τ (calculated by the method described in the following section) and the ratio τ/η are given in Tables (I–V). The plots of $\frac{T \tan \delta}{c}$ against T in some cases are shown in Figures 1, 2 and 3.

TABLE I

Toluene

6 cc of the liquid in the cell. Frequency—38.8 KMc/sec.

Temp. °C	tan $\delta \times 10^3$	$\tau \times 10^{12}$ sec.	η in c.poise	$\tau/\eta \times 10^{10}$
1	18.39	9.60	0.75	12.7
12	18.93	8.70	0.65	13.4
32	20.01	6.46	0.51	12.7
44	20.38	5.25	0.44	11.9
52	20.02	5.03	0.41	12.3
62	19.64	4.10	0.37	11.1
74	18.54	3.55	0.33	10.8
84	17.75	3.48	0.31	11.2

TABLE II

Ethyl benzene

5 cc. of the liquid in the cell Frequency—38.8 KMc/sec

Temp. °C	tan $\delta \times 10^3$	$\tau \times 10^{12}$ sec	η in c.poise	$\tau/\eta \times 10^{10}$
30	22.95	8.25	0.59	13.98
40	23.75	7.18	0.555	10.96
50	25.39	5.45	0.475	11.48
60	24.84	5.00	0.43	11.62
70	24.08	4.46	0.395	11.30
80	23.31	4.10	0.36	11.39
90	21.95	3.61	0.33	10.93
95	21.58	3.56	0.32	11.12

TABLE III

Isopropyl benzene

5 cc of the liquid in cell. Frequency—38.8 KMc/sec

Temp. °C	tan $\delta \times 10^3$	$\tau \times 10^{12}$ sec	η in c.poise	$\tau/\eta \times 10^{10}$
31	22.10	9.30	0.69	13.48
44	23.00	8.01	0.57	14.05
54	23.96	6.86	0.52	13.19
60	24.46	6.26	0.50	12.52
70	25.20	4.89	0.45	10.86
75	25.01	4.67	0.44	10.61
80	24.57	4.10	0.41	10.00
85	24.01	3.60	0.39	9.23
90	23.41	3.35	0.37	9.05
98	22.15	2.98	0.35	8.51

TABLE IV

o-Xylene

3 cc of the liquid in cell. Frequency—38.8 KMc/sec

Temp. °C	tan $\delta \times 10^3$	$\tau \times 10^{12}$ sec	η in c.poise	$\tau/\eta \times 10^{10}$
2	39.13	12.32	1.08	11.4
32	42.51	9.21	0.69	13.3
50	43.90	7.66	0.56	13.6
60	44.53	7.03	0.50	14.1
70	45.24	6.18	0.45	13.7
80	45.20	5.49	0.415	13.2
95	44.64	4.10	0.355	11.6
110	41.93	3.54	0.34	10.4

TABLE V

m-Xylene

6 cc of the liquid in cell. Frequency—38.8 KMc/sec

Temp. °C	tan $\delta \times 10^3$	$\tau \times 10^{12}$ sec	η in c.poise	$\tau/\eta \times 10^{10}$
2	13.53	12.34	0.74	15.7
17	14.32	10.56	0.64	16.5
33	14.80	9.01	0.53	17.0
54	15.08	7.68	0.43	17.8
70	15.32	6.42	0.37	17.3
80	15.54	5.50	0.34	16.2
90	15.29	5.06	0.31	16.3
98	15.13	4.10	0.29	14.1
115	13.59	2.98	0.27	11.1

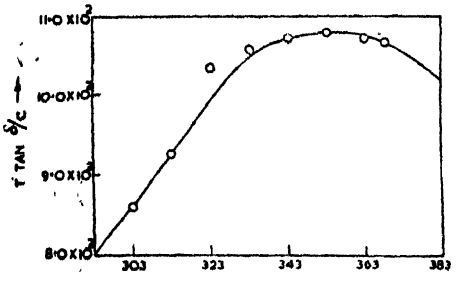

Fig. 1. Variation of T tan δ/c with T for Ethylbenzene in the liquid state.

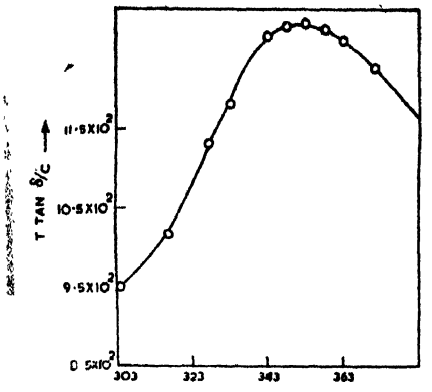

Fig. 2. Variation of T tan δ/c with T for Isopropylbenzene in the liquid state.

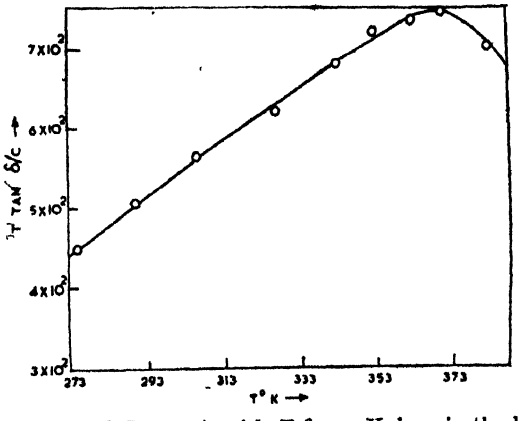

Fig. 3. Variation of T tan δ/c with T for *m*-Xylene in the liquid state.

(*a*) *Applicability of the Debye equation for dielectric loss to some polar alkyl benzenes in liquid state.*

The Debye equation for dielectric loss in the case of polar liquids is given by

$$\tan\delta = \frac{(\epsilon_1-\epsilon_0)x}{\epsilon_1+\epsilon_0 x^2} \qquad \ldots (1)$$

with $x = \frac{\epsilon_1+2}{\epsilon_0+2}\omega\tau$, where ϵ_1 and ϵ_0 are dielectric constants at static field and infinite frequency respectively. For the polar liquids studied in the present investigation $\epsilon_1 \approx \epsilon_0$ and the dipole moments being small in all the cases the internal field acting on the molecules of each liquid becomes almost equal to the externally applied field and the Debye equation reduces to the simple form (Frohlich)

$$\tan\delta = \frac{\epsilon_1-\epsilon_0}{\epsilon_1}\cdot\frac{\omega\tau}{1+\omega^2\tau^2} \qquad \ldots (2)$$

Now the polar liquids are considered as cent percent solutions in non-polar solvents (Whiffen and Thompson, 1946) and the equation (2) takes the well known form in the case of dilute solutions,

$$\tan\delta = \frac{(\epsilon+2)^2}{\epsilon} \cdot \frac{4\pi N c\mu^2}{27kT} \cdot \frac{\omega\tau}{1+\omega^2\tau^2} \qquad \ldots \quad (3)$$

where the various symbols have their usual meaning.

As τ can not be measured by any other independent method, eqn. (3) can not be used to verify directly its validity in the case of polar liquids studied in the present investigation. However, using the rate equations for viscous flow and dielectric relaxation (Whiffen and Thompson, 1946) τ may be expressed as a function of viscosity in the form $\tau = \alpha\eta^\gamma \left(\gamma = \frac{E\tau}{E\eta}\right)$ and the Debye equation (3) can be expressed as,

$$\frac{T\tan\delta}{c\mu^2} = \frac{(\epsilon+2)^2}{\epsilon} \cdot \frac{4\pi N\alpha\omega}{27k} \cdot \frac{\eta^\gamma}{1+\alpha^2\omega^2\eta^{2\gamma}} \qquad (4)$$

With suitable values of α and γ used as parameters and values of ϵ taken from literature, the L.H.S. of eqn. (4) has been plotted as a function of η for some of

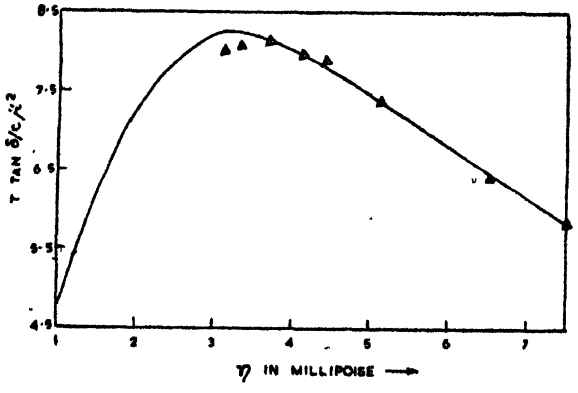

Fig. 4. Graph of $T\tan\delta/c\mu^2$ against η for Toluene. Solid line denotes theoretical curve. Δ —Experimental points.

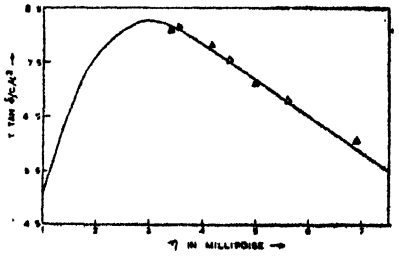

Fig. 5. Graph of $T\tan\delta/c\mu^2$ against η for *o*-Xylene. Solid line denotes theoretical curve Δ. —Experimental points.

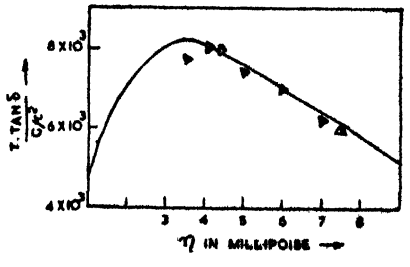

Fig. 6. Graph of $T\tan\delta/c\mu^2$ against η for Isopropylbenzene. Solid line denotes theoretical curve. Δ —Experimental points.

the compounds as shown in figures 4, 5 and 6. With experimentally observed values of tan δ and the values of μ reported by Altshuller (1954), the plots of $\frac{T \tan \delta}{c\mu^2}$ against viscosities at different temperatures are again made. It is seen that the experimental points lie very nearly on the theoretical curves in all the cases. However, the values of α are different for different compounds. The superposition of the experimental curves over the theoretical ones in the case of polar liquids under investigation shows that the modified Debye eqn. (4) for dielectric loss is valid in the case of polar liquids having dipole moments less than 1 D. However, in the present case the value of γ is taken to be unity for all the liquids. This gives a linear dependence of τ on η as is also implied in the Debye relation $\tau = 4\pi\eta a^3/kT$ and therefore, the validity of eqn. (4) may be taken to imply the validity of the Debye eqn. (3) itself.

Incidentally, it may be pointed out that since for each of the liquids only one Debye curve satisfactorily describes the dependence of dielectric loss on viscosity, only one mode of relaxation is necessary for the molecules composing each of the liquids.

(b) *Calculation of μ, τ, $E\tau$ and $E\eta$.*

The values of dipole moment μ for each of the polar liquids have been calculated from Eqn. (3) by using $\omega\tau = 1$ for the maximum of the graph of $\frac{T \tan \delta}{c}$ against T. The values of μ obtained here along with those reported by other workers (Petro and Smyth 1957; Whiffen, 1946; Altshuller 1954) are given in Table VI. The agreement is quite satisfactory. The value of τ at any temperature T has been calculated with the relation

$$\left(\frac{T \tan \delta}{c}\right)_T \Big/ \left(\frac{T \tan \delta}{c}\right)_{max} = \frac{2\omega\tau}{1+\omega^2\tau^2}$$

TABLE VI

Dipole moments in Debye unit obtained by various workers

Substance	Present authors	Petro & Smyth	Whiffen & Thompson	Altshuller
Toluene	0.30	0.31	0.32	0.31
Ethyl benzene	0.36	0.37	—	0.37
Isopropyl benzene	0.40	0.39	—	0.37
o-Xylene	0.51	0.52	0.53	0.50
m-Xylene	0.30	0.31	—	0.31

The values of τ for the compounds studied at different temperatures are given in Tables (I–V). It is seen from the Tables (I–V) that in each case τ/η is almost constant, which is different for different compounds.

The values of molar activation energy E_τ for dielectric relaxation and that for viscous flow E_η have been obtained respectively from the plots of log τ vs $1/T$

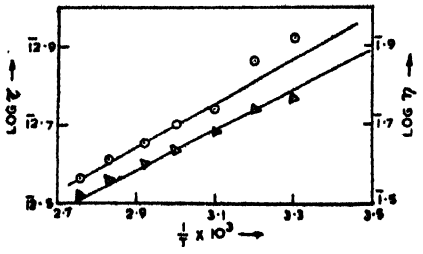

Fig. 7. Ethylbenzene
O —Plot of log $_{10}\tau$ against $1/T$.
Δ —Plot of log $_{10}\eta$ against $1/T$.

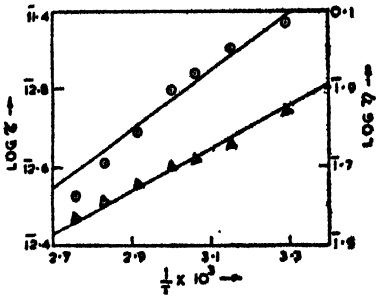

Fig. 8. Isopropylbenzene
O —Plot of log $_{10}\tau$ against $1/T$.
Δ —Plot of log $_{10}\eta$ against $1/T$.

and log η vs $1/T$ as usual (Figs. 7 and 8). The values of E_η and E_τ are given in Table VII. It is seen that in almost all the cases $E_\tau \approx E_\eta$ within experimental error. The value of the parameter $\gamma = \dfrac{E_\tau}{E_\eta} \approx 1$ used to calculate the theoretical values of $\dfrac{T \tan \delta}{c\mu^2}$ is thus justified.

It can be seen from Tables I–V that the values of time of relaxation τ for the alkyl benzenes at any temperature increase in the order of toluene < ethylbenzene < isopropylbenzene < *o*-xylene < *m*-xylene. The values of τ for toluene and *o*-xylene at different temperatures obtained in the present investigation agree well with those reported by Whiffen and Thompson (1946). But the values of τ reported by Petro and Smyth (1957) in the case of ethyl benzene, isopropylbenzene, ortho- and meta-xylenes are much different from those obtained in the present case, although the values of τ for toluene at different temperatures are almost the same in both cases. It may also be noted that the order of increase in the values of τ for toluene, ethyl benzene and isopropyl benzene are similar in both cases. The τ-values for ortho- and meta-xylenes are largest in the present investigation while those reported by Petro and Smyth (1957) are smaller than those for ethyl benzene and isopropyl benzene.

From a comparison of the values of dielectric loss (tan δ) at different temperatures for *o*-xylene, calculated from the values of ϵ' and ϵ'' given by Petro and Smyth, with those reported by Whiffen and Thompson, it is found that the tan δ values in the former case are lower by 10-15% than those in the latter case and consequently, the former τ-values are lower than the latter. Petro and Smyth used the Cole-Cole arc plot to obtain the values of critical wavelegth (λ_m) from measurements of ϵ' and ϵ'' at only two microwave ferquencies (1.25 cm and 3.22 cm). Thus the accuracy in the measurement of λ_m is very limited. Moreover, it has been observed in the present investigation that the values of λ_m

for various alkyl benzenes occur at 7.7 mm at temperatures much lower than those to be expected from the data given by Petro and Smyth. So it appears that the inaccuracy in the determination of λ_m has resulted in the inaccurate values of τ reported by them.

Petro and Smyth attempted to show that the τ-values of various benzene compounds increase in the order of their molar volumes V ($= M/d$). In the case of toluene, ethyl benzene, isopropyl benzene where the various alkyl group are substituted at the same C-atom of the benzene ring, the above correlation between τ and V has also been observed to hold qualitatively in the present investigation. But in the case of ortho-and meta-xylenes where the methyl groups are substituted at two different C-atoms of the benzene ring, even such qualitative correlation is not observed.

TABLE VII

		$\tau \times 10^{12}$ sec.	η milli-poise	$\tau/\eta \times 10^{9}$	Molar Vol. (V) cc.	Volume of the rotor in Å^3	$E\tau$ K.Cal/ mole	$E\eta$ K.Cal/ mole
Toluene	a	4.1	3.7	1.11	111.0	16.9	2.15	2.05
	b	4.6	3.8	1.21		—	1.9	2.0
	c	4.1	3.8	1.09		—	2.2	2.2
Ethyl benzene	a	5.0	4.3	1.16	127.6	17.7	2.62	2.40
	b	—	—	—		—	—	—
	c	6.2	4.4	1.57		—	2.5	2.1
Isopropyl benzene	a	6.26	5.0	1.25	145.2	19.2	3.45	2.52
	b	—	—	—		—	—	—
	c	9.8	4.9	2.00		—	3.1	2.3
o-Xylene	a	7.03	5.0	1.41	125.4	21.4	2.16	2.26
	b	6.9	5.0	1.38		—	1.9	2.3
	c	5.3	5.0	1.06		—	2.1	2.3
m-Xylene	a	7.0	4.0	1.75	127.9	26.7	1.95	1.97
	b	—	—	—		—	—	—
	c	5.3	4.1	1.30		—	2.3	2.0

a—Present authors, b—Whiffen and Thompson (1946), ad c—Petro and Smyth (1957). The values of τ, η and V given above are for 333°K in each case.

However, it is found from Table VII that the order of increase of τ-values from toluene to *m*-xylene is the same as that of the corresponding τ/η-values. By using the Debye relation $a^3 = \frac{kT}{4\pi} \cdot \tau/\eta$, the volume of the rotor at 333°K in case of each of the benzene derivatives has been calculated. These are given in Table VII along with the values of the molar volume for the respective compounds at the same temperature.

It is seen that there is no quantitative correlation between the two sets of values as regards either their relative order or their actual values. This makes

the identification of the rotor with the whole molecule uncertain. This uncertainty renders any inference about the molecular sizes and the degree of packing of the molecules in the liquid state rather unjustified. In conclusion, it is again stressed that very accurate determinations of the times relaxation for the various polar molecules in the liquid state over a wide range of temperature are necessary in order that reasonable quantitative values of certain molecular parameters may be obtained.

ACKNOWLEDGMENT

The authors wish to express their thanks to Prof. S. C. Sirkar, D.Sc., F.N.I. for helpful discussions.

REFERENCES

Altshuller, A. P., 1954, *J. Phys. Chem.*, **58**, 392.

Jenkins, H. O., 1936, *J. Chem. Soc.*, 862.

Müller, A., 1932, *Physik, Z.*, **33**, 731.

Petro, A. J. and Smyth, C. P., 1957, *J. Am. Chem. Soc.*, **79**, 6142.

Bhattacharyya, J., Sinha, B., Roy, S. B. and Kastha, G. S., 1964, *Ind. J. Phys.*, **38**, 413.

Whiffen, D. H. and Thompson, H. W., 1946, 'Dielectrics', a general discussion held by Faraday Soc., p. 122.